

CONTROLLED PROPAGATION IN ASSOCIATED MONOMER AGGREGATES

ADOLPHE CHAPIRO

*Laboratoire de Chimie des Radiations du CNRS,
92-Bellevue, France*

ABSTRACT

The polymerization of acrylic acid in bulk proceeds with a very high rate and gives rise to a syndiotactic polymer. This result is attributed to the association of monomer molecules by hydrogen bonds into linear aggregates in which a stereospecific propagation is favoured. In order to verify this assumption the polymerization of acrylic acid was investigated in various solvents. It was found that the addition of methanol, dioxane and water did not significantly affect the reaction rates nor the tacticity of the polymer. In these solvents the viscosity of the monomer remains high, suggesting that the linear aggregates are not dissociated. In contrast, the addition of toluene or *n*-hexane sharply reduces the polymerization rate and the fraction of syndiotactic polymer. The viscosity of acrylic acid also drops in the presence of these solvents. These results are in agreement with the assumption that the polymerization of acrylic acid is strongly controlled by linear monomer aggregates.

A similar situation is believed to apply to acrylamide. The propagation rate constant of this monomer was found to vary widely depending on the solvent used. This could indicate that the propagation rate is governed by monomer aggregates, the extent of aggregation being a function of the nature of the solvent. Methacrylic acid behaves in a different manner. This monomer forms the same types of associations as acrylic acid but the polymerization kinetics do not reflect any peculiarities related to such aggregates.

A very strict control of chain propagation is met when 4-vinylpyridine is polymerized in the presence of polycarboxylic acids. A considerable rate increase was observed when vinylpyridine was grafted into polytetrafluoroethylene films which contained poly(acrylic acid) branches. This effect is accounted for by assuming that the pyridine substituents associate with the carboxylic groups, thereby providing a very favourable orientation of the vinyl groups for chain propagation.

Several polymerization studies conducted in this laboratory have led to unusual kinetic features which are correlated with the association of monomer molecules resulting in ordered aggregates. The purpose of the present communication is to summarize these results and to stress some of the similarities or differences observed in the various systems.

I. BULK AND SOLUTION POLYMERIZATION OF ACRYLIC ACID

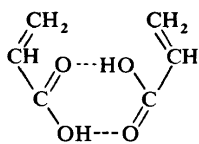
Earlier work in this laboratory¹ has shown that when pure acrylic acid is

subjected to gamma radiation at room temperature a very rapid polymerization ensues which leads to a syndiotactic polymer of extremely high molecular weight ($M_v = 1$ to 3×10^7). The stereoregular polymer is easily separated from the atactic isomer (virtually absent in bulk polymerization) by solvent extraction: the atactic polymer being soluble in anhydrous dioxane while the syndiotactic material only dissolves when 20 per cent water is added to this solvent. An insoluble gel is left as a residue after extraction. The stereoregular polymer readily crystallizes to fairly large single crystals. It is noteworthy that the syndiotacticity remains unaltered for polymerizations carried out at 20° , 40° , 60° or 76° .

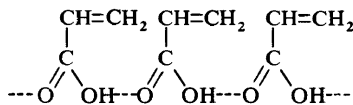
(1) Monomer aggregates in acrylic acid

In order to explain these findings it was assumed that these peculiar features of the polymerization of acrylic acid are related to the fact that this monomer forms associated structures via hydrogen bonding. It is well established² that carboxylic acids form cyclic dimers. Originally, the dimeric structures such as I were believed to be responsible for the stereospecific propagation. Such structures can be assumed to exhibit planar symmetry and one can indeed expect that the simultaneous reaction of two monomer molecules having this configuration would lead to a syndiotactic diad.

Alternatively, one can assume that the monomer forms linear aggregates of type II. In such an event, the double bonds lie in a narrow zone and on encounter with a growing chain the addition of the first monomer molecule



(I)



(II)

could be followed by a 'zip' reaction involving all monomer units of the aggregate. This would account for the very high rate of propagation found in this system and eventually for the syndiotacticity of the polymer, provided the double bonds are properly oriented.

Very little information is available in the literature on such associations in carboxylic acids. Dimeric structures of type I are characterized in dilute solutions²; linear structures of type II have also been reported^{3,4}.

(2) Viscosity of acrylic acid solutions

The presence of linear aggregates of type II should give rise to an increased viscosity. A study was therefore carried out on the viscosity of acrylic acid in bulk and in various solvents which were believed to interfere with hydrogen bonding⁵⁻⁷. Some of the results are presented in *Figure 1* which shows the flow times of various binary mixtures as a function of the concentration of acrylic acid.

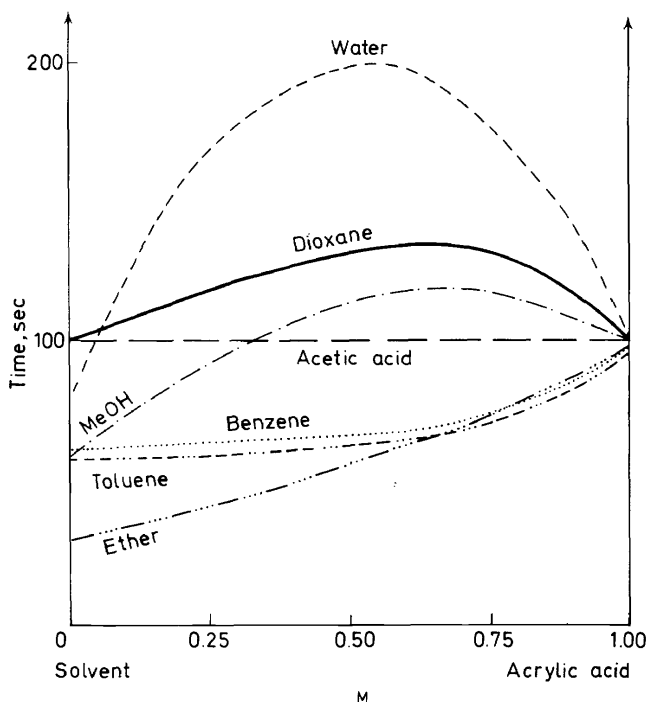


Figure 1. Flow times of acrylic acid in various solvents as a function of monomer content^{6,7}

The pure monomer exhibits high viscosity, higher than that of water which is known to have a polymeric structure. The addition of methanol, dioxane or water leads to an increase in flow time and a maximum appears which is particularly pronounced in the case of water. Acetic acid has approximately the same flow time as acrylic acid and in the mixtures the viscosity remains constant. In toluene, ether and *n*-hexane, the viscosity drops and all experimental points lie below the linear relationship which corresponds to a simple dilution effect. These results are further discussed below.

(3) Polymerization kinetics of acrylic acid in solutions

Poly(acrylic acid) is insoluble in its monomer; consequently, the polymerization in bulk occurs in a precipitating medium and exhibits the usual kinetic anomalies associated with such reactions. Water, methanol and dioxane dissolve the polymer and, hence, upon addition of these compounds the reaction medium gradually changes from a heterogeneous to a homogeneous one. The kinetic features associated with this change in the case of methanol have been described earlier⁵. Figure 2 shows the rate data obtained with water solutions. A pronounced maximum appears at a concentration of ca. 50 per cent monomer. The molecular weights of the polymer exhibit a maximum for the same concentration (Figure 3) which indicates a particularly

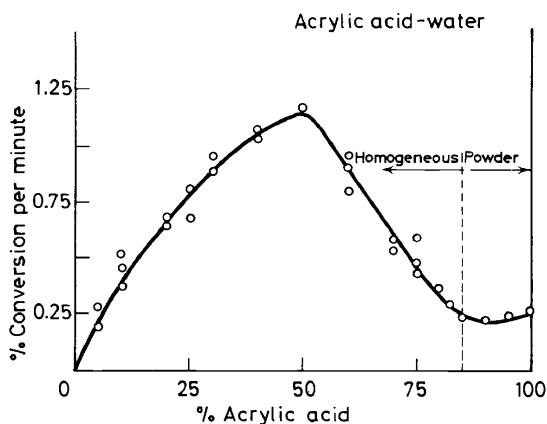


Figure 2. Rate of polymerization of acrylic acid in aqueous solutions as a function of monomer concentration. Initiation by gamma rays (16 rads/min) at 20°C⁷

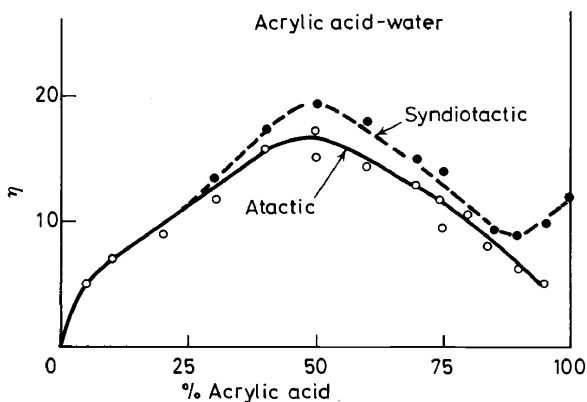


Figure 3. Limiting viscosity indexes of syndiotactic and atactic fractions of poly(acrylic acid) obtained in aqueous solutions at different monomer concentrations⁷

favourable propagation to termination ratio in this mixture, in which the polymer forms a viscous solution (gel effect).

It should be noted that the polymerization rate hardly changes upon the addition of up to 20 per cent solvent. A similar result is obtained with methanol, dioxane and acetic acid. In contrast, in the presence of small amounts of toluene and *n*-hexane the rates and molecular weights are drastically reduced. Some of the data are presented in Figure 4.

The above results show a striking correlation between the polymerization rates and the viscosities of the initial solutions: only those solvents which reduce the viscosity of acrylic acid also reduce the reaction rates.

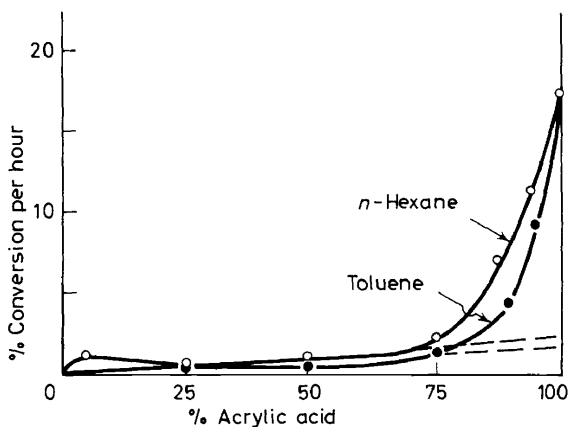


Figure 4. Rate of polymerization of acrylic acid in toluene and *n*-hexane solutions as a function of monomer concentration. Initiation by gamma rays (12 rads/min) at 20°C

(4) Tacticity of the resulting polymer

In these experiments all reaction products were fractionated by solvent extraction as described above in order to determine the relative amounts of atactic and syndiotactic polymer.

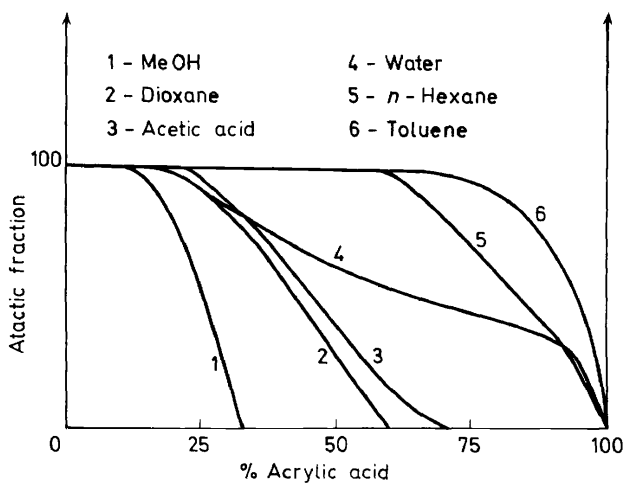


Figure 5. Amount of atactic fraction in the poly(acrylic acid) obtained from various solutions as a function of monomer content in polymerizing mixture⁷. 1 Methanol, 2 Dioxane, 3 Acetic acid, 4 Water, 5 *n*-Hexane, 6 Toluene

Figure 5 shows the results obtained in the various solutions investigated as a function of monomer content. It can be seen that syndiotactic polymer is formed in methanol, dioxane acetic acid and water solutions up to fairly

high dilutions (50 to 70 per cent solvent) whereas in toluene and *n*-hexane only atactic polymer arises when more than 20 per cent solvent is added to the monomer.

The various results presented above conform with the assumption that the polymerization of acrylic acid in concentrated media is governed by linear monomer aggregates of type II. These are responsible for the high rate of the reaction and for the formation of syndiotactic poly(acrylic acid). Methanol, dioxane and water do not seem to destroy these linear structures and the fact that the viscosities of these solutions exhibit maxima suggests that these solvents superimpose their own associated structure on to that of acrylic acid and perhaps link several linear aggregates together. This new structure neither significantly affects the rates nor the tacticity of the polymer.

In contrast, non-polar solvents such as toluene and *n*-hexane destroy the linear associations of acrylic acid as indicated by the drop in viscosity (*Figure 1*). Infra-red data⁷ suggest that in these solutions the linear structures of type II are converted to the dimeric form I. Under such conditions the rate of propagation is strongly reduced and the resulting polymer is atactic. In order to account for the high viscosity of acrylic acid and for the peculiar kinetic features of its polymerization, the linear association aggregates should contain on the average at least 20 to 50 monomer molecules and the lifetime of such aggregates should be reasonably long. Experiments are in progress to gain direct evidence for the presence and of the characteristics of such linear aggregates in acrylic acid.

II. OTHER SYSTEMS

(1) Acrylamide

The free radical polymerization of acrylamide has been studied by several authors⁸⁻¹¹. Most experiments were carried out in aqueous solutions and extremely long kinetic chains were observed. On the other hand, the determination of the rate constants for chain propagation (k_p) and termination (k_t) led to the surprising result that both k_p and k_t strongly depended on the solvents used for the reaction medium¹¹. Some of the results are summarized in *Table 1*.

Table 1. Rate constants in the polymerization of acrylamide at 19°C¹¹

| Solvent | $k_p \times 10^{-4}$ moles l ⁻¹ sec ⁻¹ | E_p kcal mole ⁻¹ | $k_t \times 10^{-7}$ moles l ⁻¹ sec ⁻¹ | E_t kcal mole ⁻¹ |
|--------------------|---|----------------------------------|---|----------------------------------|
| Water (pH = 7) | 9.4 | 2.7 | 7.2 | 2.7 |
| Water (pH = 13) | 4.3 | 3.6 | 1.7 | 1.0 |
| Formamide | 0.9 | 5.0 | 2.1 | 0.8 |
| Dimethylsulphoxide | 0.27 | 5.4 | 2.5 | 0 |

In order to interpret the very high k_p value observed in aqueous media the authors¹¹ assumed that the double bond of the monomer became protonated in water, thus increasing the reactivity of the monomer in this solvent.

Alternatively, the results can be accounted for, as with acrylic acid, by assuming the formation of linear aggregates of type I. The length and stability of these aggregates would depend on solvent–monomer interactions and could thus explain the observed results, if indeed such aggregates occur preferentially in water. Experiments are in progress to verify these assumptions¹².

(2) Methacrylic acid

Methacrylic acid, like acrylic acid, forms linear aggregates in the bulk liquid as indicated by its high viscosity. Dilution of the monomer in various solvents leads to a pattern similar to that shown in *Figure 1* for acrylic acid^{13,14}. The polymerization of methacrylic acid occurs, however, much more slowly than that of acrylic acid under similar experimental conditions. *Figure 6* shows a comparison of the rates observed with both monomers at

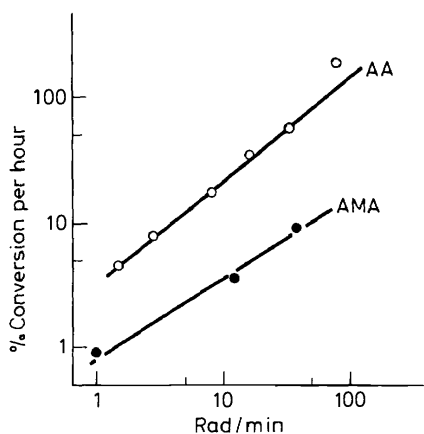


Figure 6. Rates of polymerization of acrylic (AA) and methacrylic acids (AMA) at 20°C as a function of dose rate of gamma rays¹³

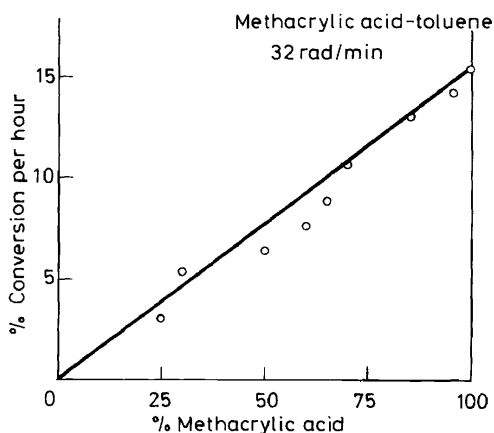


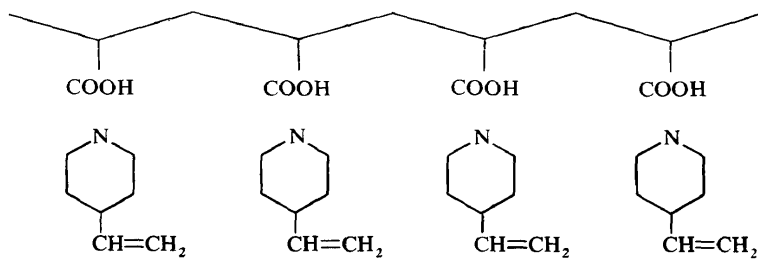
Figure 7. Rate of polymerization of methacrylic acid in toluene solutions as a function of monomer concentration. Initiation by gamma rays (32 rads/min) at 20°C¹⁴

different dose rates¹³. Moreover, the resulting poly(methacrylic acid) does not exhibit any striking stereoregularity. These results indicate that although linear aggregates of type I are present in this monomer they do not play a major role in controlling the polymerization. This conclusion is substantiated by experiments carried out in toluene solutions¹⁴. *Figure 7* shows that the addition of toluene to methacrylic acid results in a linear decrease of the polymerization rate, in striking contrast to the results obtained with acrylic acid (*Figure 4*). It thus appears that the destruction of linear aggregates by toluene (as shown by the drop in the viscosity of these solutions) does not significantly affect the polymerization kinetics of methacrylic acid.

The reason for such different behaviour of two very similar monomers is not clear. It is possible that the methyl group in the methacrylic derivative prevents by some steric or 'hydrophobic' action the alignment of the monomer molecules to form the favourable configuration for fast chain propagation and stereospecific control. This point requires further experimental support.

(3) Polymerization of vinyl pyridine in the presence of polyacids

Kabanov *et al.*¹⁵ have shown that the polymerization of vinyl pyridine in the presence of polycarboxylic or polysulphonic acids is controlled by a regular arrangement of the monomer molecules which can be schematically represented by structure III.



(III)

Here again the double bonds of the monomer appear to come into close contact thus favouring a fast propagation reaction involving properly oriented monomer molecules in the aggregate.

We have met a similar situation in our work on the preparation of semi-permeable membranes containing both carboxylic and pyridine groups. The technique involved the grafting in a first step of acrylic acid into polytetrafluoroethylene films by gamma irradiation; the resulting carboxylic membranes are thereafter neutralized by potassium hydroxide and grafted in a second step with 4-vinylpyridine¹⁶. The treatment by KOH is required in order to prevent the spontaneous polymerization of vinylpyridine, presumably initiated by proton transfer¹⁵.

In these experiments it was found that in the presence of poly(potassium acrylate) branches, vinylpyridine polymerized several orders of magnitude faster than in the ungrafted PTFE films¹⁷. Some results are summarized in *Table 2*.

CONTROLLED PROPAGATION IN ASSOCIATED MONOMER AGGREGATES

Table 2. Rates of grafting of 4-vinylpyridine into PTFE films containing various amounts of grafted acrylic acid; gamma-rays of 48 rads/min at 20°C¹⁷

| Acrylic acid in initial PTFE film (%) | Time required to reach 100% grafting | Total dose (rads) |
|---|---|----------------------|
| 0 | 48 hours | 138000 |
| 16 | 21 min | 1000 |
| 23 | 14 min | 670 |
| 35 | less than 6 min | less than 300 |

It can be seen that the increase in rate in the presence of polycarboxylic branches is considerable. An extremely small radiation dose leads to very high grafting ratios, thus indicating very long kinetic chains. From the observation that no polymerization is observed in the absence of irradiation, provided the carboxylic groups are converted to the potassium salt, it can be concluded that the increase in rate is entirely due to faster chain propagation, presumably due to a 'zip' propagation process similar to that postulated in the bulk polymerization of acrylic acid.

It should be noted that the complexed aggregates of structure III seem to be much more efficient in increasing the polymerization rate than the linear structure of type II in acrylic acid. If one assumes that the rate of polymerization of acrylic acid in toluene or *n*-hexane solutions is that of the 'normal' reaction not involving any ordered aggregate, one can estimate this 'normal' rate by extrapolating the low rate region of the curves to the pure monomer as shown in *Figure 4*. This procedure leads to values which suggest that the linear aggregates are responsible for an increase in rate not exceeding a factor of seven to ten. In contrast, the data presented in *Table 2* show that the structure of type III is responsible for much larger increases in rate. One reason for the difference in order of magnitude of these effects lies presumably in the fact that structures of type III are *permanent* and presumably involve most monomer molecules present in the system, whereas structures of type II are *transient*. The linear aggregates are in dynamic equilibrium with the dimeric structure I, thus their effective lifetime is presumably short. Moreover, only a small fraction of the monomer molecules is likely to be involved in structures such as II, most carboxylic groups being associated as cyclic dimers.

CONCLUSION

The results discussed above indicate that associated monomer aggregates may affect polymerization kinetics in many different ways. Linear structures in which the monomer is associated by hydrogen bonds may either accelerate the polymerization as with acrylic acid and perhaps acrylamide or have no significant effect like in methacrylic acid. It is noteworthy that in acrylic acid such structures are presumably responsible for a stereospecific propagation. On the other hand, complexed structures such as schematically shown in III are permanent matrices which lead to much higher rate increases. Steric control of propagation is also expected to arise in such matrices provided

the proper configuration of the double bonds is reached in the corresponding complex.

REFERENCES

- ¹ A. Chapiro and T. Sommerlatte, *Europ. Polym. J.* **5**, 707 and 725 (1969).
- ² G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond*, Freeman : (1960).
- ³ E. Constant and A. Lebrun, *J. Chim. Phys.* **61**, 163 (1964).
- ⁴ J. Lascombe, M. Haurie and M. L. Josien, *J. Chim. Phys.* **59**, 1233 (1962).
- ⁵ A. Chapiro and F. Laborie, *C.R. Acad. Sci., Paris*, **267**, 1110 (1968).
- ⁶ A. Chapiro, *Plastiques Modernes et Elastomères* **23**, No. 5, 154 (1971).
- ⁷ A. Chapiro, J. Dulieu and F. Laborie, *3rd Internat. Symp. Radiation Chemistry, Tihany* (1971).
- ⁸ C. E. Schildknecht, *Vinyl and Related Polymers*, pp 317-322. Wiley : New York (1952).
- ⁹ D. G. Currie, F. S. Dainton and W. S. Watt, *Polymer (London)*, **6**, 451 (1965).
- ¹⁰ V. F. Gromov, A. V. Matveeva, A. D. Abkin, P. M. Khomikovskii and E. I. Mirokhina, *Dokl. Akad. Nauk SSSR*, **179**, 374 (1967).
- ¹¹ V. F. Gromov, P. M. Khomikovskii and A. D. Abkin, *Vysokomol. Soedin.* **12**, 767 (1970).
- ¹² L. Perec, Unpublished results.
- ¹³ A. Chapiro and Nguyen-Thi Tuyet-Hao, *J. Chim. Phys.* **68**, 1070 (1971).
- ¹⁴ Lê Thi-Nhi, Unpublished results.
- ¹⁵ V. A. Kabanov, V. A. Petrovskaya and V. A. Kargin, *Vysokomol. Soedin. Ser. A*, **10**, 925 (1968).
- ¹⁶ A. Chapiro, G. Bex, A. M. Jendrychowska-Bonamour and T. O'Neill, *Advanc. Chem. Ser.* **91**, 560 (1969).
- ¹⁷ A. Chapiro and A. M. Jendrychowska-Bonamour, *C.R. Acad. Sci., Paris*, **270**, 27 (1970).